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16. ABSTRACT

A formalism is presented for calculating the ambient concentration of secondary sulfate at any downwind distance from an SO_2-emitting point source. The SO_2 is assumed to be affected by dispersion, dry deposition and homogeneous gas-phase oxidation processes having arbitrary time dependences. A receptor model estimate of the primary particle contribution at the downwind site is used to account for all of the dispersion and part of the deposition. An important finding is that the secondary sulfate is sensitive only to the average values of the deposition and oxidation rates, and not to their detailed time dependences. Extensions of the formalism to include wet deposition and nitrate formation are also discussed.

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HYBRID RECEPTOR MODEL FOR SECONDARY SULFATE FROM AN SO_2 POINT SOURCE

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Abstract—A formalism is presented for calculating the ambient concentration of secondary sulfate downwind (100–200 km maximum) from an SO_2 point source. The SO_2 is assumed to be affected by dispersion, dry deposition and homogeneous gas phase oxidation processes having arbitrary time dependences. A receptor model estimate of the primary particle contribution at the downwind site is used to account for all of the dispersion and part of the deposition. It is shown that the secondary sulfate is sensitive only to the average values of the deposition and oxidation rates, and not to their detailed time dependences.

Key word index: Hybrid receptor model, tracer elements, secondary sulphate.

INTRODUCTION

The traditional method for developing ambient air pollution control strategies has been the source oriented or dispersion model approach. This method uses a mathematical dispersion model, coupled with meteorological information and a source emissions inventory, to calculate how the source emissions become distributed throughout the surrounding region. It is increasingly recognized, however, that receptor oriented models provide a viable alternative in addressing the control strategy problem. Such models assess the contributions from various sources by using primarily measurements made at the ambient (receptor) site, with meteorological and source emissions information of secondary importance.

Classical aerosol receptor methods are primary (particles that reach the receptor site are assumed to have been emitted as particles by a source) and conservative (particles are assumed to have undergone no chemical transformation between source and receptor) in character. Thus, a classical receptor method cannot readily deal with the substantial portion of fine particle ambient mass which is known to be secondary in nature, such as the sulfate resulting from SO_2 transformation in the atmosphere. Recently, Friedlander (1981) suggested one approach to incorporating reactive species within a receptor model framework, which was applied to the source apportionment of polycyclic aromatic hydrocarbons in Los Angeles. In the following, a different reactive species receptor theory is presented, for the specific application of calculating secondary sulfate from an SO_2 point source. Such an application, of course, has considerable interest in the context of current research on the sources of acid precipitation. The resulting expression for secondary sulfate concentration M_{SO_4} will be seen to have a factored structure of the form

$$M_{SO_4} = M_p A T, \tag{1}$$

with M_p being the mass concentration at the receptor of primary fine particles from the source (calculated from a classical receptor model), A representing the ratio of source mass emission rates for SO_2 and fine particles and T describing both the transformation of SO_2 to sulfate in the atmosphere and its loss due to deposition. A 'hybrid receptor model' refers to a source apportionment procedure which uses not only data characteristic of receptor models (ambient measurements), but also information generally associated with dispersion models (emissions rates or meteorological data). Equation (1) is describable in such terms, since the quantity M_p is obtained from ambient measurements, while A and T depend on emissions rates and meteorological data (wind speed and direction) for their evaluation.

We anticipate that the range of applicability of the proposed model is up to distances of 100–200 km, i.e. over a mesoscale range. Such an estimate is based on several considerations: (a) the ambient concentrations of the source tracer elements from which M_p in Equation (1) is calculated, must not become so dilute as to be indistinguishable from background levels or below measurable limits; (b) particle fractionation effects during transport, due to differing size distributions of the chemical species, will increase with transport distance; (c) estimates of plume 'age' t, required for T in Equation (1), become less certain as the distance from the source increases and (d) mesoscale distances allow for non-negligible amounts of SO_2 to be transformed to sulfate but may be small enough (depending on the spatial separation of the sources) to avoid the complexity and greater uncertainty of dealing with multiple SO_2 sources.

THEORY

1. *Ambient sulfate and* SO_2

Consider an air parcel emitted at time $t = 0$ by a single point source. We wish to determine the changing concentrations of SO_2, fine particle sulfate (primary and secondary), and all other primary fine particles within the parcel as it is transported along a Lagrangian trajectory to a downwind receptor site. During transport the pollutants are simultaneously affected by dispersion, deposition, and transformation. We make the following assumptions: (1) all three processes are linear or pseudo first-order processes but may have complex dependences on time; (2) dispersion affects all three categories of pollutants in an identical manner; (3) dry deposition is the only type of deposition which occurs; (4) deposition affects all the fine particles in an identical manner, but may be different for SO_2 and (5) secondary sulfate is produced only by the homogeneous gas phase oxidation of SO_2.

Several comments on these assumptions are in order. The linearity assumption is a common one (Ozkaynak and Ryan, 1982), but allowance for arbitrary time dependences improves upon the frequent simplification of fixed rate constants. Assuming gas phase oxidation of SO_2 is a pseudo first-order process is supported by the experimental work of Clark *et al.* (1976) and Miller (1978). Nonetheless the validity of this assumption is currently an important controversial issue. If the assumption of equal dispersions for gas and particles is to have any validity, it is of course essential that only fine particles (aerodynamic diameter of order 1 μm or less) be included. This is the reason for considering only the fine component of the primary particle emissions. It is also well to note that secondary sulfate is consistent with this since it is well known that its production from SO_2 and subsequent growth process largely restrict it to the sub-μm size range (Whitby, 1978). Allowing for a difference in dry deposition rates between SO_2 and sulfate reflects the customary view that the dry deposition velocity (to which the deposition rate is proportional) for SO_2 is an order of magnitude greater than that of sulfate (Olson *et al.*, 1982). Finally, the assumptions exclude wet deposition, and oxidation by aqueous-phase and heterogeneous processes, which can be important in some circumstances.

With the above assumptions we have

$$dM_p/dt = -k M_p \tag{2}$$

$$dM_{SO_2}/dt = -k_r M_{SO_2} - k_d M_{SO_2} - k M_{SO_2} \tag{3}$$

$$dM_{SO_4}/dt = +\frac{3}{2} k_r M_{SO_2} - k M_{SO_4} \tag{4}$$

where

t = air parcel 'age' [h],
$M_p(t)$ = concentration [$\mu g\, m^{-3}$] at time t of primary fine aerosol,
$M_{SO_2}(t)$ = concentration [$\mu g\, m^{-3}$] at time t of SO_2,
$M_{SO_4}(t)$ = concentration [$\mu g\, m^{-3}$] at time t of total sulfate (primary and secondary),
$k_r(t)$ = pseudo first-order reaction rate [$\%\ h^{-1}$] at time t for $SO_2 \rightarrow$ sulfate,
$k(t)$ = total (dispersion + deposition) removal rate [$\%\ h^{-1}$] at time t for either primary fine particles or secondary sulfate and
$k_d(t)$ = *additional* deposition loss rate [$\%\ h^{-1}$] at time t for SO_2.

The plume age t is approximately the ratio of the source–receptor distance to the average wind speed. This ignores meandering of the parcel, but is reasonable for wind speeds greater than a few m s^{-1}, and for the mesoscale range assumed. The required average wind speed may be determined by subjective and objective analysis of surface and upper air meteorological data available from routine meteorological monitoring programs (e.g. NOAA National Climatic Center). The most accurate determination, however, would be through pilot balloon (pibal) observations made concurrently with the field sampling (Clarke, private comm., 1984).

Equations (2)–(4) may be solved successively, giving the exact solutions

$$M_{SO_2} = M_p A(0) \exp[-(\bar{k}_r + \bar{k}_d)t] \tag{5}$$

$$M_{SO_4} = \frac{3}{2} M_p A(0) T + M_p B(0) \tag{6}$$

where

$$T = \int_0^t k_r \exp\left[-\int_0^{t'} (k_r + k_d)\, dt''\right] dt' \tag{7}$$

$$A(0) = M_{SO_2}(0)/M_p(0) \tag{8}$$

$$B(0) = M_{SO_4}(0)/M_p(0) \tag{9}$$

$$\bar{k}_r = \frac{1}{t}\int_0^t k_r\, dt' \tag{10}$$

and an expression for $\bar{k}_d$ analogous to Equation (10). So long as $t = 0$ corresponds to the time at which the air parcel is emitted at the source, then $A(0)$ and $B(0)$ can be written in terms of emission rate ratios

$$A(0) = \frac{\text{mass emission rate [g s}^{-1}\text{] of SO}_2}{\text{mass emission rate [g s}^{-1}\text{] of primary fine particles}} \tag{11}$$

$$B(0) = \frac{\text{mass emission rate [g s}^{-1}\text{] of primary sulfate}}{\text{mass emission rate [g s}^{-1}\text{] of primary fine particles}} \tag{12}$$

The transformation/deposition factor T given by (7), while exact, has a complicated appearance which makes it difficult to understand its essential structure. In the Appendix T is shown to be well approximated by

the expression

$$\bar{T} = \frac{\bar{k}_t}{\bar{k}_t + \bar{k}_d}\left[1 - \exp\left(-(\bar{k}_t + \bar{k}_d)t\right)\right] \qquad (13)$$

giving the much simpler result

$$M_{SO_4} = \frac{3}{2} M_p A(0) \frac{\bar{k}_t}{\bar{k}_t + \bar{k}_d}\left[1 - \exp \times \left(-(\bar{k}_t + \bar{k}_d)t\right)\right] + M_p B(0). \qquad (14)$$

Equation (14) has several important features: (1) most of the dispersion/deposition complexity is not required to be known since it is already contained in M_p; (2) deposition and transformation are uncoupled and may be estimated independently; (3) $SO_2 \rightarrow$ sulfate transformation rates (and also dry deposition rates) having radically different time dependences but equal average values will result in the same amount of secondary sulfate. The insensitivity to details of the rates' time dependences, except as they influence the average values, is a significant simplification which mirrors an analogous result in dispersion theory (Lamb, 1980); (4) secondary sulfate production is only weakly dependent on the differential deposition loss of SO_2 (a first order expansion in t of (14) does not depend on $\bar{k}_d$ at all). This is discussed more quantitatively in Section 3.

2. *Estimates for* $\bar{k}_t$ *and* $\bar{k}_d$

There is an extensive literature of reported values for average SO_2 transformation and deposition rates from plume studies (primarily power plants), which is inappropriate to summarize here. As first estimates we suggest the values of 1 and 2 %$\,h^{-1}$ for $\bar{k}_t$ and $\bar{k}_d$, respectively. Ozkaynak and Ryan (1982) obtained these values (to be understood as 24-h averages) from sulfate and SO_2 measurements taken from the SURE data base. They are generally consistent with those of other investigators (Husar *et al.*, 1978) under dry summer conditions. Depending on the availability of additional information, these estimates may be refined in various ways.

One such possibility for $\bar{k}_t$ is the parametrization proposed by Gillani *et al.* (1981)

$$\bar{k}_t[\%\,h^{-1}] = 0.03\,R\,\Delta z\,[O_3]_0, \qquad (15)$$

where R is the solar insolation (kW m^{-2}), Δz the vertical plume spread (m), and $[O_3]_0$ the background O_3 concentration (ppm). The three factors can be seen as surrogates of reaction excitation, plume dilution and oxidant availability, respectively. It is useful to note that virtually all estimates of $\bar{k}_t$ based on plume measurements (for example, the Gillani result) have been extracted under the assumption of a linear transformation rate. This means that the resulting value is a 'lumped' parameter which at least partially compensates for non-linear influences. Thus, when such an estimate is re-used in a linear model, such as the present one, some benefit of the non-linear compensation is retained provided that the concentrations of the oxidizing species in the region where the model is to be applied are not significantly different from those in the area where the pseudo-first order rate constant was derived.

Refinement of $\bar{k}_d$ could include the influences of season, land-use type, atmospheric stability class, and diurnal variation, as for example has been done in the dry deposition module included in the dispersion model ENAMAP-2S (Endlich *et al.*, 1983).

The difficulty of obtaining accurate values of $\bar{k}_t$ and $\bar{k}_d$ for use in (5) and (14) should not be minimized. However, neither the basic problem nor its difficulty is changed whether the traditional dispersion approach or the present receptor method is chosen.

3. *Sensitivity analysis*

How much do the uncertainties in the variables of Equation (14) affect the accuracy with which M_{SO_4} can be calculated? Assuming independence of the errors ΔX_i in each variable X_i, the standard propagation of errors procedure leads to a relative error in M_{SO_4} given by

$$\frac{\Delta M_{SO_4}}{M_{SO_4}} = \left[\sum\left(\frac{\partial M_{SO_4}}{\partial X_i}\frac{\Delta X_i}{M_{SO_4}}\right)^2\right]^{1/2}. \qquad (16)$$

Evaluation of (16) requires numerical choices for $\bar{k}_t$, $\bar{k}_d$ and $B(0)/A(0)$. We take these to be 1, 2, and 3 %$\,h^{-1}$, respectively, from Ozkaynak and Ryan (1982), obtained from the SURE data base and emissions inventory. In addition, we assume the relative uncertainty $\Delta X_i/X_i$ for each variable to be 20 %. The results may be easily scaled to any other uncertainty value of choice.

Each solid graph in Fig. 1 labelled by a variable X_i shows

$$\left|\frac{\partial M_{SO_4}}{\partial X_i}\frac{\Delta X_i}{M_{SO_4}}\right|,$$

i.e. the contribution each variable's uncertainty makes to the relative uncertainty in M_{SO_4}. The dotted graph is the total relative error in M_{SO_4}, i.e. (16). Corresponding results for the relative uncertainty in predicted SO_2 concentrations are shown in Fig. 2. The graphs of Figs 1 and 2 cover a larger range of t than what is likely to be appropriate in practice (for a mesoscale range—assuming 200 km and an average windspeed of 3 m s^{-1} – t is under 20 h).

There are interesting contrasts between Figs 1 and 2. While the sulfate total uncertainty beyond 10 h is quite constant around 34 %, the SO_2 total uncertainty steadily increases with time. Not surprisingly the relative importances of the SO_2 transformation and deposition rate uncertainties in the overall SO_2 and sulfate concentration uncertainties are reversed between the two cases. The plume age uncertainty is of decreasing importance beyond several hours for the sulfate total uncertainty, but the plume age uncertainty eventually becomes the dominant component of the SO_2 total uncertainty. Finally, it is apparent that the primary sulfate emissions uncertainty has negligible impact beyond several hours.

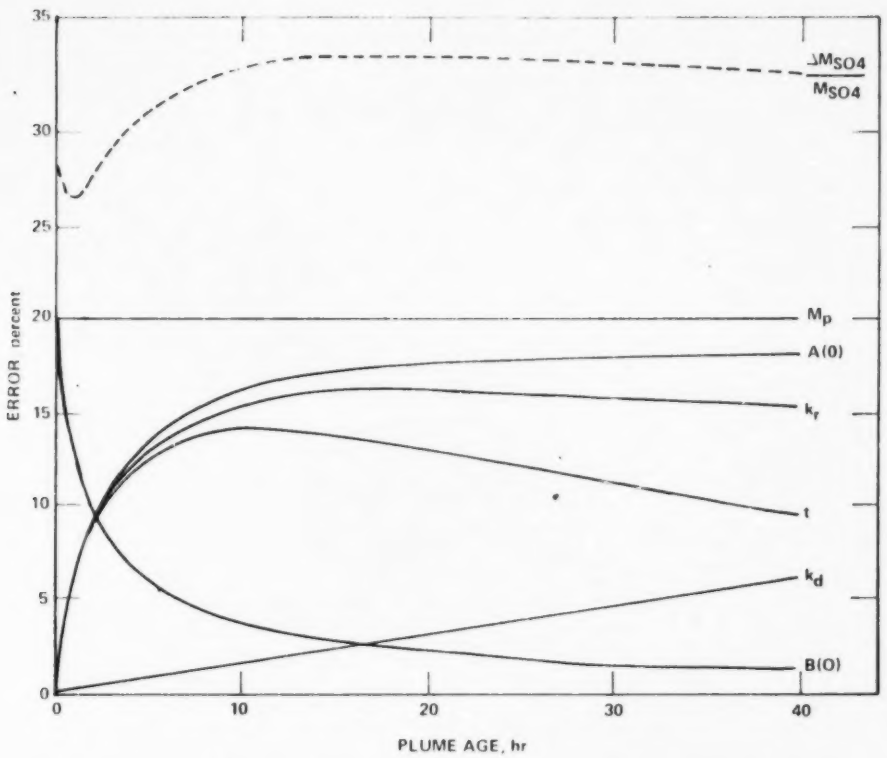

Fig. 1. Total percentage uncertainty in M_{SO_4} (dotted graph), and portion of total percentage uncertainty contributed by each variable (solid graphs), vs plume age. The relative uncertainty in each variable is assumed to be 20%.

4. *Inverse solution:* $\bar{k}_r$ *and* $\bar{k}_d$

Equations (5) and (14) predict the downwind concentrations of SO_2 and sulfate from a single SO_2 source, if the average transformation and differential dry deposition rates ($\bar{k}_r$ and $\bar{k}_d$) were known or could be estimated. Because of their simple structure, it is an easy matter to invert the equations, thus obtaining

$$\bar{k}_r t = \frac{1}{X} \ln Y \tag{17}$$

and

$$\bar{k}_d / \bar{k}_r = X - 1 \tag{18}$$

where

$$X = \frac{3}{2}[A(0) - A(t)]/[B(t) - B(0)] \tag{19}$$

and

$$Y = A(0)/A(t). \tag{20}$$

The quantities $A(t)$ and $B(t)$ are respectively SO_2 and sulfate ratios similar to $A(0)$ and $B(0)$ given by Equations (8) and (9) except for their evaluation at time $t \neq 0$.

There are two alternatives in employing Equations (17)–(20). If $t = 0$ corresponds to the time of emission, then $A(0)$ and $B(0)$ can be expressed in terms of emission rate ratios according to Equations (11) and (12), and $A(t)$ and $B(t)$ would be evaluated from plume measurements of SO_2 and sulfate concentrations at a downwind distance corresponding to the plume age t. Alternatively, $t = 0$ may be associated with any arbitrary downwind distance from the source. In this case $A(0)$ and $B(0)$ would be obtained from the appropriate pollutant concentrations measured at that distance, just as $A(t)$ and $B(t)$ are obtained from concentrations at a more distant point. When Equation (17) is regarded in terms of the latter alternative, it is the same as a relationship that has been employed in previous plume studies (Easter *et al.*, 1980), except that the A and B ratios were defined in terms of an artificial tracer, SF_6, instead of the 'natural tracer' M_p used here.

Equations (17) and (18) on the one hand, and Equations (5) and (14) on the other, are opposite but equivalent solutions to the same problem, i.e. determining the relationships between the quantities that influence the downwind concentration of SO_2 and sulfate from a single point source. Clearly, the same data set cannot be used both to predict SO_2 and sulfate concentrations, and also estimate values for $\bar{k}_r$ and $\bar{k}_d$. Whether the 'inverse' or 'normal' solution is preferred depends entirely on one's objective.

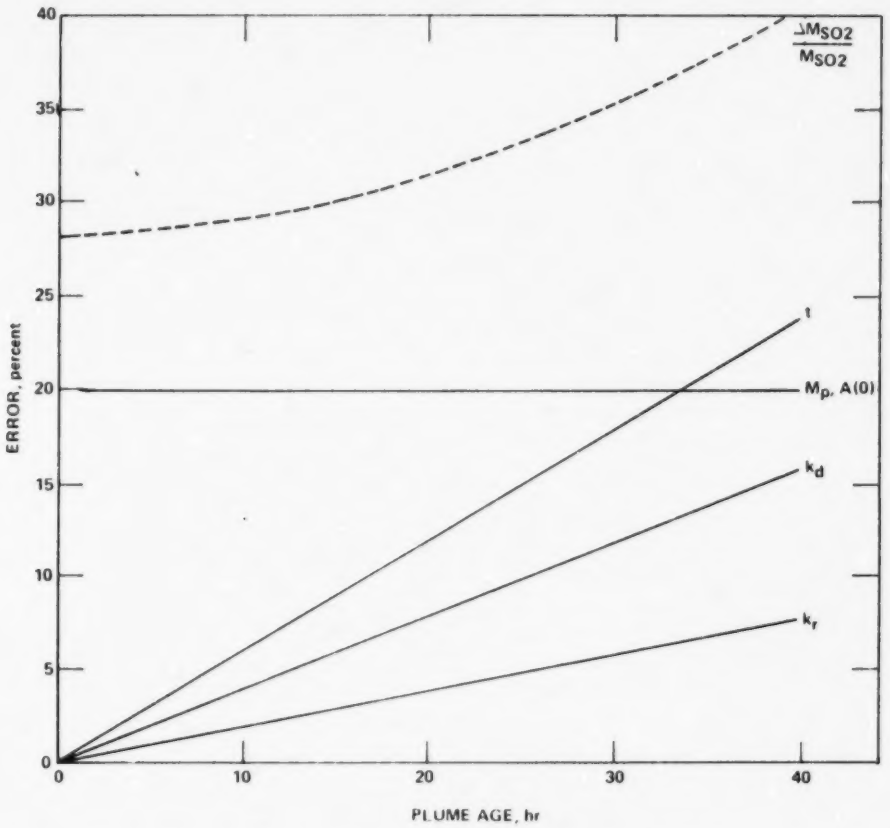

Fig. 2. Total percentage uncertainty in M_{SO_4} (dotted graph), and portion of total percentage uncertainty contributed by each variable (solid graphs), vs plume age. The relative uncertainty in each variable is assumed to be 20%.

While Equations (17)–(20) are simple in appearance, their use in a field situation may be difficult: measurements of SO_2 and sulfate concentrations at the receptor site may contain contributions from sources other than the single one of interest. If so, the additional contributions would need to be estimated by moving the samplers in and out of the plume in the case of airborne sampling, or by comparing concentrations measured by fixed samplers located both in and out of the plume.

5. *Determination of* M_p

The presence of M_p in Equation (14) means that a prediction of secondary sulfate must be preceded by a conventional receptor model calculation to estimate the mass concentration at the receptor of the primary fine particles from the source of interest. The two general approaches that can be employed for this purpose are the Chemical Mass Balance (CMB) and multivariate methods. The former assumes a knowledge of the profiles (i.e. listings of the average chemical composition, in $mg\,g^{-1}$, of the primary particle emissions) of all the sources that significantly contribute to the fine particle ambient mass concentration at the receptor site. In contrast, the latter uses the variation of elemental species concentrations in a large number of successive samples measured at the receptor, to both identify the contributing sources and estimate their impacts (the M_p's). Henry *et al.* (1984) have given a comprehensive review of the several techniques, some of considerable sophistication, that are included in both approaches.

The two approaches can be illustrated by the single element tracer technique, the simplest and still one of the most used methods of receptor modeling. This technique assumes that for each (SO_2) source of interest a single element (or chemical species) can be found which is emitted by that source but by no other that is a contributor to the receptor site. Then the primary impact of the source of interest is given by

$$M_p = M_i/a_i, \tag{21}$$

where M_i is the mass concentration of the tracer element measured at the receptor site and a_i is the

tracer element's fractional contribution to the source's primary emissions. Within a CMB framework a_i is obtained from a direct emissions measurement at the source. In contrast, a multivariate method would determine $1/a_i$ as a coefficient in a multiple linear regression (Kleinman *et al.*, 1980).

There are a number of candidate elemental aerosol tracers for the major SO_2 emission source types. For coal combustion, of which electric power plants are the major sources, Se and As have long been suggested as key tracers. For example, it has been estimated that 62% of the anthropogenic Se emitted into the atmosphere comes from coal burning (National Research Council, 1976). The work of Wangen (1981) emphasizes the potential usefulness of Ba as well as supporting the Se choice at least in short distance transport. For transport over at least a mesoscale range, Stevens *et al.* (1984) and Tuncel *et al.* (1985) have shown a strong correlation between fine sulfate and Se, using back trajectories to associate this with coal combustion origins. For oil combustion V and, less frequently, Ni have been used as tracers. For various non-ferrous metal smelters the metals themselves (Cu, Zn, etc.) would be prime candidates.

Regrettably very few reliable measurements of the a_i's required in Equation (21) exist for SO_2 sources. This is because the best tracer elements are frequently in the vapor phase when exiting the stack at the high temperatures characteristic of these sources, but quickly condense in the atmosphere to form fine particle aerosol. Most stack samplers were not designed to take account to this, and consequently measure erroneously low values for a_i. The dilution-size segregating source sampler developed by Houck *et al.* (1982), was designed to address the volatility (and size fractionation) limitations of earlier source sampling methods. The scarcity of reliable source measured a_i values of course enhances the appeal of obtaining these values with a multivariate approach.

Finally, it is worthwhile to consider the advantages of restricting the measurement of the primary aerosol to particle sizes even smaller than the 'fine fraction' ($\leq 2.5\ \mu m$) of a dichotomous sampler. Emissions measurements at western U.S. coal-fired power plants have shown a large (10–200) enrichment of several elements including Se in the particle size range below $0.3\ \mu m$ (Biermann and Ondov, 1980; Wangen, 1981). Restricting the sampled aerosol to a sub-μm range may provide not only a sharper signature of the source, but because of the reduced particle size heterogeneity, will also better satisfy the model's assumption that primary aerosol, SO_2, and transformed sulfate are identical in their dispersion characteristics.

CONCLUSIONS

Equation (14), giving the ambient concentrations of primary and secondary sulfate from a single SO_2 source, is the principal result of this study. While its dependence on the average values of transformation and deposition rates (rather than their detailed time behaviors) has a seemingly familiar appearance, this feature is a derived consequence instead of an initial assumption as in the usual derivation. Estimates are given for the degree of approximation involved in Equation (14) compared with the exact solution, as well as its parameter sensitivity. Throughout guidance in the estimation of parameter values is also given, concluding with a discussion of the single element tracer technique as an illustration of receptor methods for determining the parameter M_p.

We readily acknowledge that a portion of what has been presented is not new; many of the elements have appeared separately in previous work, but in contexts such that their connections with receptor modeling has not been very obvious. The availability of these elements in an integrated form should be of interest in the planning of field measurements aimed at determining the origins of secondary sulfate, by emphasizing which parameters must be measured and the measurement accuracy that is required.

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REFERENCES

Biermann A. H. and Ondov J. M. (1980) Application of surface-deposition models to size-fractionated coal fly ash. *Atmospheric Environment* **14**, 289–295.

Clark W. E., Landis D. A. and Harker A. B. (1976) Measurements of the photochemical production of aerosols in ambient air near a freeway for a range of SO_2 concentrations. *Atmospheric Environment* **10**, 637–644.

Easter R. C. *et al.* (1980) Plume conversion rates in the SURE region. Volume 1. EPRI Report No. EA-1498, Palo Alto CA 94304.

Endlich R. M., Nitz K. C., Brodzinsky R. and Bhumralkar C. M. (1983) The ENAMAP-2 air pollution model for long-range transport of sulfur and nitrogen compounds. U.S. Environmental Protection Agency Final Report for Contract No. 68-02-3424, Research Triangle Park, NC.

Friedlander S. K. (1981) New developments in receptor modeling theory. In *Atmospheric Aerosol: Source, Air Quality Relationships* (edited by Macias E. S. and Hopke P. K.), pp. 1–19. ACS Symp. Series No. 167, American Chemical Society, Washington, D.C.

Gillani N. V., Kohli S. and Wilson W. E. (1981) Gas-to-particle conversion of sulfur in power plant plumes—I. Parametrization of the conversion rate for dry, moderately polluted ambient conditions. *Atmospheric Environment* **15**, 2293–2313.

Henry R. C., Lewis C. W., Hopke P. K. and Williamson H. J.

(1984) Review of receptor model fundamentals. *Atmospheric Environment* **18,** 1507–1515.
Houck J. E., Cooper J. A. and Larson E. R. (1982) Dilution sampling for chemical receptor source fingerprinting. Paper 82-61M.2 Air Pollution Control Association 75th Annual Meeting, June 20–25, 1982, New Orleans, LA.
Husar, R. B., Patterson D. E., Husar J. D. and Gillani N. V. (1978) Sulfur budget of a power plant plume. *Atmospheric Environment* **12,** 549–568.
Kleinman M. T., Pasternack B. S., Eisenbud M. and Kneip T. J. (1980) Identifying and estimating the relative importance of sources of airborne particulates. *Envir. Sci. Technol.* **14,** 62–65.
Lamb R. G. (1980) Mathematical principles of turbulent diffusion modeling. In *Developments in Atmospheric Science* (edited by Longhetto A.), Vol. 11, pp. 173–210. Elsevier, New York.
Miller D. F. (1978) Precursor effects on SO_2 oxidation. *Atmospheric Environment* **12,** 273–280.
National Research Council (1976) Selenium. Medical and Biologic Effects of Environmental Pollutants Series, Nat. Acad. Sci., Washington, D.C.
Olson M. P., Voldner E. C. and Oikawa K. K. (1982) A computed sulphur budget for the eastern Canadian provinces. *Wat. Air Soil Pollut.* **18,** 139–155.
Ozkaynak H. and Ryan P. B. (1982) Modeling of pollutant transport and removal during a regional sulfate episode. *Wat. Air Soil Pollut.* **18,** 157–171.
Stevens R. K., Dzubay T. G., Lewis C. W and Shaw R. W. (1984) Source apportionment methods applied to the determination of the origin of ambient aerosols that affect visibility in forested areas. *Atmospheric Environment* **18,** 261–272.
Tuncel S. G., Olmez I., Parrington J. R., Gordon G. E. and Stevens R. K. (1985) Composition of fine particle regional sulfate component in Shenandoah Valley *Envir. Sci. Technol.* (in press).
Wangen L. E. (1981) Elemental composition of size-fractionated aerosols associated with a coal-fired power plant plume and background. *Envir. Sci. Technol.* **15,** 1080–1088.
Whitby K. T. (1978) The physical characteristics of sulfur aerosols. *Atmospheric Environment* **12,** 135–159.

APPENDIX

A mathematical transformation of Equation (7) gives the identity

$$T = \bar{T} + \Delta T \tag{A1}$$

where $\bar{T}$ is given by Equation (13) and

$$\Delta T = \frac{1}{\bar{k}_r + \bar{k}_d} \int_0^t (\bar{k}_d k_r - \bar{k}_r k_d) \exp\left[-\int_0^{t'} (k_r + k_d) dt'' \right] dt'. \tag{A2}$$

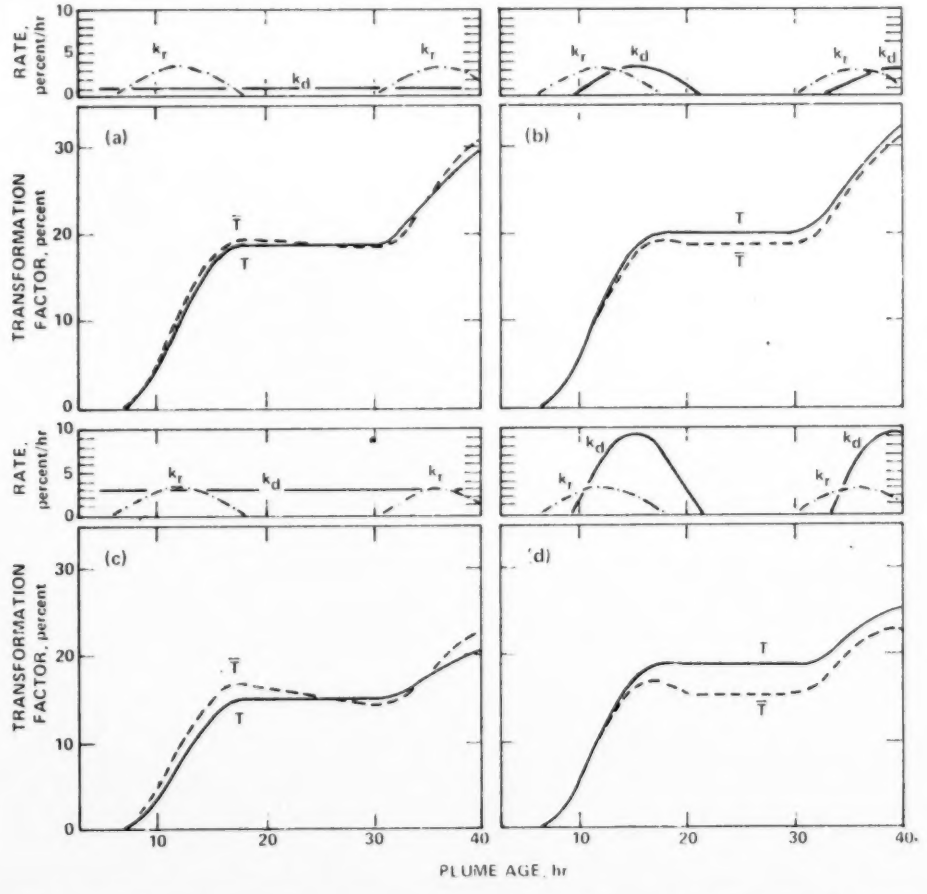

Fig. 3. Comparison of T and $\bar{T}$ vs plume age t for four choices of transformation and deposition rate functions, $k_r(t)$ and $k_d(t)$. For any 24-h period $\bar{k}_d = 0.01\ h^{-1}$ (a) and (b), $\bar{k}_d = 0.03\ h^{-1}$ (c) and (d), $\bar{k}_r = 0.01\ h^{-1}$ (a)–(d).

What are the conditions under which ΔT is small in comparison to $\bar{T}$? While this question does not have a simple answer in general we note that $\Delta T = 0$ when k_r and k_d are proportional but otherwise arbitrary. This is a useful observation since k_r and k_d are generally regarded as having similar diurnal trends (attaining a maximum during midday hours and dropping to low values at night), thus approximately proportional.

To explore this in quantitative terms T and $\bar{T}$ were calculated using four different choices of the rates $k_r(t)$ and $k_d(t)$ having magnitudes and time dependences that were considered appropriate according to current knowledge. Each quadrant of Fig. 3 shows the comparisons between T and $\bar{T}$ for the k_r and k_d choice sketched in the upper part of the quadrant. All four cases correspond to midnight being the time of emission ($t = 0$). In Figs 3(a) and (c) constant values are chosen for k_d. In Figs 3(b) and (d), k_d is represented by the positive lobe of a sine function between 9 a.m. and 9 p.m., and zero during the remaining times. For all four cases the same time dependence for k_r is assumed: the positive lobe of a sine function between 6 a.m. and 6 p.m., and zero during the remaining times. The use of sine representations for k_r and k_d is intended to simulate diurnal behaviors. The 3-h shift between their maxima has no particular basis; coincident maxima would of course result in $T = \bar{T}$. For any 24-h averaging period the amplitudes of k_r and k_d are such that $\bar{k}_d = 0.01\ h^{-1}$ in Figs 3(a) and (b), $\bar{k}_d = 0.03\ h^{-1}$ in Figs 3(c) and (d), and $\bar{k}_r = 0.01\ h^{-1}$ throughout.

From Figs 3(a)–(d) we find the maximum percentage deviation $(T-\bar{T})/T$ to be 4, 6, 13 and 17%, respectively. Alternatively, every calculation of T and $\bar{T}$ represented in Fig. 3 is consistent with the inequality

$$|T-\bar{T}|/T \leq 0.063\,\bar{k}_d/\bar{k}_r. \qquad \text{(A3)}$$

We suggest that inequality (A3) is a useful rule of thumb in estimating how well $\bar{T}$ approximates T in any situation that is likely to arise.

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